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Size distribution of EC and OC in the aerosol of Alpine valleys during summer and winter

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Abstract. Collections of samples were conducted for the determination of the size distributions of EC and OC during the intensive sampling campaigns of the POVA program, in two Alpine valleys of the French Alps, in summer and in winter. The comparison of concentrations obtained for samples collected in parallel with impactor- and filter-based methods is rather positive with slopes of 0.95 and 0.76 for OC and EC, respectively and correlations close to 1 (0.92 and 0.90 for OC and EC, respectively, $n=26$). This is an indication that the correction of pyrolysis seems to work for the impactor samples despite non even deposits. The size distributions of the concentrations of EC and OC present large evolutions between winter and summer, and between a suburban and a rural site. In winter, an overwhelming proportion of the mass fraction of both species is found in the droplet and accumulation modes, often (but not always) in association with sulfate and other chemical species resulting from secondary formation processes. Some indications of gas/particles exchanges can be found for the other parts of the size spectrum (the Aitken and super micron modes) in the case of the rural site. In summer, the changes are more drastic with, according to the case, a dominant droplet or accumulation mode. Particularly at the rural site, the large extent of processing of the aerosol due to gas/particles exchanges is evident for the Aitken and super micron modes, with increasing of the OC mass fractions in these size ranges. All of these observations give indications on the degree of internal vs. external mixing of the species investigated in the different modes.

1 Introduction

Few studies have focused on the size distribution of the carbonaceous fraction (Elemental Carbon (EC) and Organic Carbon (OC)) of atmospheric particles, even though this characteristic is probably of the utmost importance for aspects related to global climate (Kanakidou et al., 2004 and references therein), the impact of aerosols on human health (Turpin, 1999; Dreher, 2000), and the understanding of the formation processes of the particles containing these compounds (Kerminen and Wexler, 1995). Several investigations are currently available in the literature that outline studies conducted in different environments (Viidanoja et al., 2002, and references therein). However, the number of samples in most of these studies is rather low, and the consistency of the sampling and analytical methods not proven.

The program POVA (Pollution des Vallées Alpines) was launched in 2000 to focus on atmospheric chemistry in the two transit corridors between France and Italy: the Chamonix and Maurienne Valleys. This study was timed to take advantage of a unique opportunity: the “Tunnel du Mont Blanc” (TMB) in the Chamonix Valley was closed for nearly 3 years after a large accident in March 1999. During this time period, most of the heavy-duty traffic in the area was re-routed through the “Tunnel du Fréjus”, in the Maurienne Valley. The general goal of the POVA program was to compare the air quality and modelled atmospheric emissions and transport in these two valleys before and after the re-opening of the TMB to heavy-duty traffic. The program included several intensive field campaigns, a long-term campaign, and 3-D modelling of atmospheric dynamics and chemistry (Brulfert et al., 2005).

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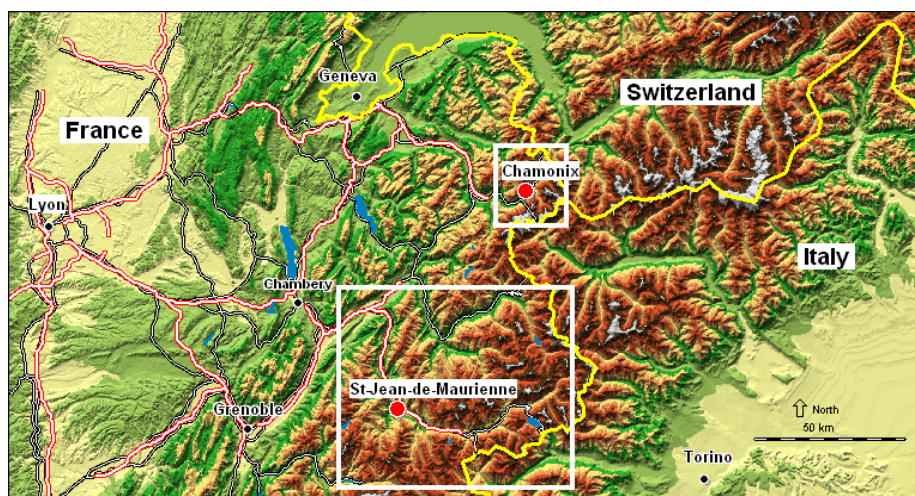


Fig. 1. Sampling areas in the French Alps.

We proposed other publications that present discussions on the seasonal evolutions of concentrations of EC, OC, and WSOC in the aerosol obtained during the long term campaign (Aymoz, 2005; Jaffrezo et al., 2005a, b¹). In this paper, we are presenting results of EC and OC measurements conducted on samples obtained in parallel with impactor and open face filter samplings during two intensive sampling campaigns, at one site in each valley. First, we are aiming at a comparison of the concentrations obtained with these two sampling methods, to evaluate the validity of impactor sampling and analysis for the determination of the size distribution of EC and OC concentrations. In a second part, we are considering the changes in size distributions of EC and OC concentrations according to the site (suburban or semi rural) and the season (winter or summer). One of the questions is to figure out if the results are coherent with our current knowledge of the formation and evolution processes of the carbonaceous fraction of the aerosol and, then, if the size distributions measured can bring more information on these processes.

2 Experimental

2.1 Sampling sites

One site was located in the Chamonix valley (Fig. 1). This valley is 23 km in length, closed at its lower end by a narrow gorge (the Cluses pass) and at the upper end by the Col des Montets (1464 m a.s.l.) leading to Switzerland. The valley is rather narrow (1 to 2 km on average at the bottom). The

elevation of the valley floor is approximately 1000 m a.s.l. on average, and is surrounded by tall mountains culminating in the summit of Mont Blanc (4807 m a.s.l.). There are no industrial emissions or waste incinerators in the valley, and the main anthropogenic sources of emissions are vehicular traffic, residential heating (typically fuel or wood-burning stoves), and some agricultural activity. The permanent population of about 12 000 is augmented by tourism, which brings in many times that number (on average 100 000 person/day in summer, and about 5 million overnight stays per year), mainly for short-term visits. There is only one road supporting all of the traffic into and out of the valley, but many secondary roads spread over the valley floor and the lower slopes. During the closing of the TMB leading to Italy, the traffic at the entrance of the valley (14 400 vehicles/day on average) consisted mainly of cars (91% of the total, 50% of which were powered by diesel), along with a small number of local trucks (5%) and tourist buses (1%). Natural sources of emissions are limited to forested areas, which are mainly composed of coniferous species (95% of which consists of spruce, larch and fir). Re-suspension of soil dust is limited in winter, as most of the ground surface is covered by snow. The sampling site was located in a residential area of the Chamonix town (6.86019° E; 45.9143° N; altitude 1034 m a.s.l.), in an open grassy area about 50 m from a secondary street. It can therefore be considered as an urban background site.

The second site was located in the Maurienne Valley, in the small village of Orelle (6.56670° E; 45.2101° N; altitude 1134 m a.s.l.), about 20 km up valley from the main town of Saint Jean de Maurienne (Fig. 1). The Maurienne Valley is much longer (about 80 km in length) and wider (about 3–5 km on average at the valley floor) than the Chamonix Valley. The surrounding mountains are lower, peaking at 3852 m a.s.l. with La Grande Casse. The elevation at the mouth of the valley is 330 m a.s.l. and increases to

¹Jaffrezo, J.-L., Aymoz, G., Cozic, J., Chapuis, D., and Maenhaut, W.: Seasonal variation of PM₁₀ main constituents in two valleys of the French Alps. I: EC/OC fractions, *Atmos. Chem. Phys. Discuss.*, in preparation, 2005b.

Table 1. Dates of the two intensive sampling campaigns, and number of samples and field blanks collected during each sampling week.

Winter 2003		
Chamonix	From Wednesday 15/01/2003 08:00 6 impactor samples for EC/OC and 7 blanks 6 impactor samples for ionic components and 6 blanks 39 filters for EC/OC and 6 blanks	To Wednesday 22/01/2003 08:00
Maurienne	From Friday 24/01/2003 08:00 7 impactor samples for EC/OC and 7 blanks 7 impactor samples for ionic components and 7 blanks 36 filters for EC/OC and 5 blanks	To Friday 31/01/2003 08:00
Summer 2003		
Maurienne	From Wednesday 25/06/2003 08:00 6 impactor samples for EC/OC and 7 blanks 6 impactor samples for ionic components and 7 blanks 42 filters for EC/OC and 7 blanks	To Wednesday 02/07/2003 08:00
Chamonix	From Friday 04/07/2003 08:00 7 impactor samples for EC/OC and 7 blanks 7 impactor samples for ionic components and 7 blanks 41 filters for EC/OC and 7 blanks	To Friday 11/07/2003 08:00

2081 m a.s.l. at the end of the valley (the Col du Mont Cenis, leading to Italy). The topography of the Maurienne Valley is more complex than that of Chamonix, and includes many tributary valleys and several narrow gorges and sharp bends. The 30 km of the lower valley up to the town of Saint Jean de Maurienne supports several heavy industries, including steel transformation and aluminium and phosphorus production. Other anthropogenic emissions are linked to traffic. Most traffic (95% of the trucks and 55% of the cars) is found on the 50 km of highway leading from the valley entrance up to the town of Modane, the location of the entrance of the “Tunnel du Fréjus” leading to Italy. The traffic through the valley during the closure of the TMB averaged about 11 500 vehicles/day at Saint Jean de Maurienne, with 38% consisting of heavy-duty diesel trucks. The valley also supports agricultural activities, and some large forested areas, of which 60% consists of deciduous species (beech and chestnut) and the remaining 40% being occupied by coniferous trees (spruce). The total population of the valley is represented by about 45 000 inhabitants, most of whom are concentrated in the lower 40 km. Tourism is not as important as in Chamonix, but it results in about 4.2 million overnight stays per year on average, mostly during the winter season and in the upper part of the valley, where several ski resorts are located. The sampling also took place on an open grassy area in the Orelle défilé, and the location can be considered a rural site, but is largely influenced by the highway and industrial emissions from the lower part of the valley.

2.2 Sampling and processing

Samplings were conducted during two intensive sampling campaigns (ISCs) in winter (from 15 January to 31 January 2003) and summer (from 25 June to 11 July 2003), each time for a full week successively in each valley (Table 1). First, total aerosol samples were collected with open face filter holders (47 mm in diameter, average flow rate at $1.54 \text{ m}^3 \text{ hr}^{-1}$, face velocity of 36 cm s^{-1}) for EC and OC analyses. This was maintained continuously on 4-h intervals (starting at 08:00 local time) during the full weeks. Second, daily sampling (starting at 08:00 LT) for the determination of EC, OC and ionic concentrations according to the aerosol size distribution were maintained with 2 separate 13-stage Dekati impactors operating at flow rates of 30 l min^{-1} . The size cut diameters ($D_{50\%}$) of the 13 stages are 0.030; 0.060; 0.108; 0.17; 0.26; 0.40; 0.65; 1.0; 1.6; 2.5; 4.4; 6.8; and $10.0 \mu\text{m}$, respectively. Air intakes for all of these collection devices were located 4 m above ground on the platform of scaffolding. Field blanks (i.e., exposed filters without any air filtration) were collected daily for all these series. The number of samples and field blanks for all these series are presented in Table 1.

We used Gelmann Teflon Zefluor filters (porosity $1 \mu\text{m}$) for the determination of concentrations of ionic species. They were cleaned before use with a couple of bathes of methanol (Baker C-MOS grade). We used QMA Whatman filters for the determination of EC and OC concentrations, for both the total filtration and impactor samplings. Before use, these filters were fired for 1 h at 800°C to lower

Table 2. Concentrations in the field blanks for the chemical species presented (units are ng/m³/stage for impactors, and ng/m³ for filters, using typical volumes of sampling).

	Clos Winter	Clos Summer	Orelle Winter	Orelle Summer
Impactor				
EC	< 1	< 1	< 1	< 1
OC	64.3±47.8	7.0±1.8	18.0±19.8	16.8±10.0
Filters				
EC	< 1	< 1	< 1	< 1
OC	47.2±32.7	388.4±313.6	77.0±6.5	291.1±50.1
Impactor				
Sulfate	0.3±0.3	0.5±0.1	0.4±0.2	0.7±0.3
Nitrate	0.6±0.6	< 0.1	2.9±1.8	0.3±0.3
Potassium	0.3±0.2	0.1±0.1	0.2±0.2	0.1±0.1
Calcium	0.4±0.3	0.5±0.5	1.0±0.6	0.8±0.4

the blank levels for EC and OC. All of these filters were kept and transported to the field in packs of 20 in leak-proof glass jars before sampling. After sampling, exposed filters were immediately downloaded in the field in a laminar flow hood and stored at −5°C in individual petri slides wrapped in aluminium foil in sealed bags, until the analysis. All handling procedures were designed to reduce potential contaminations.

2.3 Analysis for EC and OC

Samples were analyzed for EC and OC using the Thermo-Optical Transmission (TOT) method on a Sunset Lab analyzer (Birch and Cary, 1996). We used temperatures up to 870°C for the analysis of OC in 100% He, and up to 900°C for the analysis of EC in 98% He+2% O₂ (Aymoz, 2005; Jaffrezo et al., 2005a). Automatic split time was always used for the distinction between EC and pyrolysed OC, except for blank samples, where it was manually corrected when needed. We analyzed a fraction of 1.5 cm² from each sample of the total aerosol sampling, without any preparation. The impactor samples were analyzed in full after removing their outer ring (in contact with holders) with scalpels. The arithmetic average of the concentrations of the field blanks for each weekly series (Table 2) was taken into account for the calculation of atmospheric concentrations of that specific series, both for total filters and impactors.

2.4 Analysis of ionic species

The series of samples from the second impactor sampling were analyzed with Ionic Chromatography (IC) for the determination of a whole suite of anionic and cationic species following the method described in Jaffrezo et al. (1998), Riccard et al. (2002), and Aymoz (2005). In brief, samples were soaked in 7.4 ml of Milli-Q water for 30 min in airtight glass

bottles, after wetting them with 0.6 ml of methanol (C-MOS grade, Baker). The extract was then filtered just before the analysis using Acrodisc filters (Pall Gelmann) with a porosity of 0.2 µm. Analysis of cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) took place with a CS12 column on a Dionex 100 IC. Analysis of inorganic anions (Cl[−], NO₃[−], SO₄^{2−}) and dicarboxylic acids (DCA) (oxalate, glutarate, malonate, succinate, malate, and tartrate) took place on an AS11 column on a Dionex 500 IC. We will only present some of the results from these series in this paper, in relation with the interpretation of the EC and OC evolutions of the size distributions. Table 2 presents the detection limits for these last species under the conditions of our analysis.

3 Comparison of results for EC and OC

On top of the questions linked to the potential positive/negative sampling artefacts related to the semi volatile nature of many compounds composing OC (Viidanoja et al., 2002; Eatough et al., 2003), the main problem in the determination of EC and OC size distributions in aerosol samples is the correction of the pyrolysed fraction of OC during TOT or TOR (Thermo Optical Reflectance) analyses of the carbonaceous fraction, for impactor sampling that lead to non uniform deposits on the sampling substrates. Therefore, most of the results from previous studies using impactors for the determination of the size distribution of carbonaceous species are presented as total carbon concentrations (Temesi et al., 2003), with collection on aluminium substrates. Some other studies are presenting EC and OC values obtained in such conditions, making the assumption that the pyrolysed fraction is low (Cabada et al., 2004). To the best of our knowledge, only Viidanoja et al. (2002) proposed an evaluation of the results obtained with quartz filters for impactor sampling, using the ability of the TOT method to deliver a proper correction of the pyrolysed fraction in this case. They showed that for sampling with a SDI impactor (i.e. with very compact deposits) and an analysis with a TOT method (with an OC part using temperature up to 900°C), the use of the pyrolysis correction lead to a severe underestimation of EC concentrations compared to those obtained with filter sampling with a virtual impactor. However, this study consists in a few samples only (n=14), collected in only one season in Finland (late spring from May to mid July). It is therefore interesting to further test such a method, with different conditions and a larger set of samples.

We can first compare the results obtained during our study for the TC measurements, for the series obtained for total filter and impactor sampling. For the overall data set (summer and winter, urban and rural samples), the regression between the two series is:

$$[TC_{\text{impactor}}] = 0.92 * [TC_{\text{totalfilter}}] - 0.69$$

$$R^2 = 0.94; \quad n = 26 \quad (\text{concentrations in } \mu\text{g}/\text{m}^3).$$

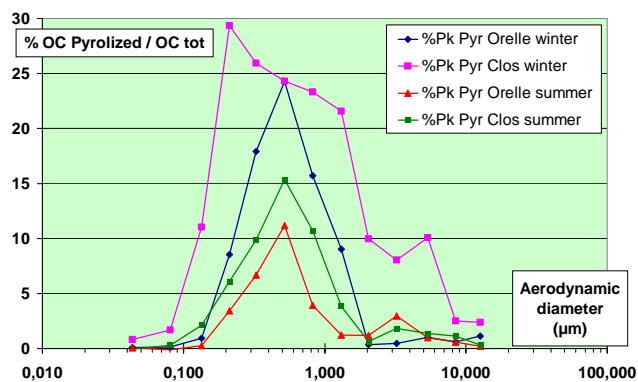


Fig. 2. Average size distribution of the pyrolysed OC contribution to total OC for all of the campaigns.

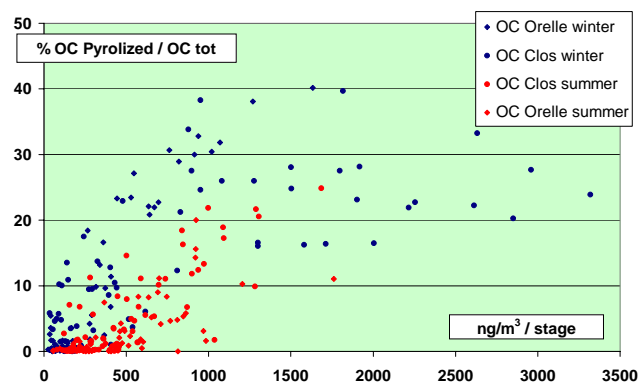


Fig. 3. Contribution of the pyrolysed OC to total OC for all samples according to the total OC sample loading.

It indicates a slight underestimation for the impactor sampling that can potentially be attributed to larger adsorption artefacts of the semi volatile organic compounds (SVOC) with the filter sampling. This is corroborated in our data by the much lower value in summer of the average ratio of TC concentrations between the two series: 0.59 ± 0.10 in summer (when the concentrations of SVOC is supposedly maximum) as opposed to 1.07 ± 0.23 in winter. The results obtained by ten Brink et al. (2004) during the INTERCOMP 2000 experiment, with also a low slope of 0.73, may indeed be due to very large differences in the adsorption artefacts between quartz filters and aluminium substrates (for the impactor sampling) (R. Hitzenberger, personal communication, 2005).

Then, we can try to evaluate the relevance of the TOT method for the determination of EC and OC concentrations for impactor sampling. Figure 2 presents the size distributions of the pyrolysed OC contribution to total OC, averaged for all of the 6 or 7 samples of each campaign in our study. It shows that the amount of the pyrolysed fraction presents some large degree of organization according to the

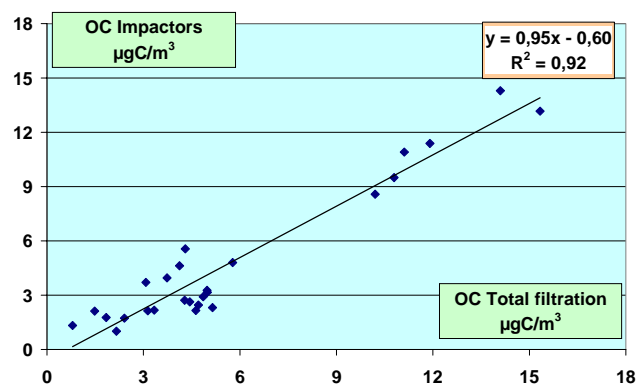


Fig. 4. Comparison of daily OC concentrations obtained with the impactor and total filtration sampling for all campaigns.

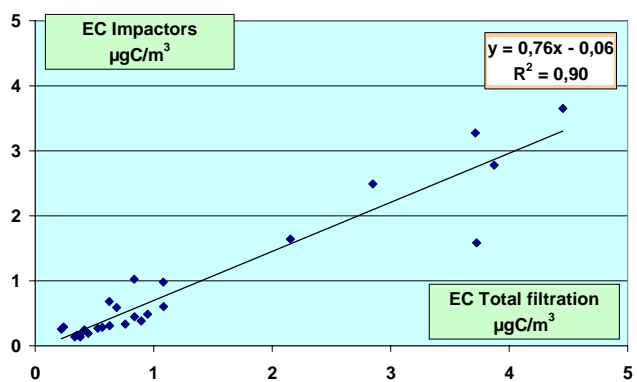


Fig. 5. Comparison of daily EC concentrations obtained with the impactor and total filtration sampling for all campaigns.

size range, the sampling site, and the season, and is not randomly distributed as could be expected if it was highly dependant upon the respective location of the sample deposits and of the laser beam during the thermal analysis. However, such a pattern could be partly induced by a strong link between this pyrolysed amount and the total amount of OC (Yu et al., 2002), since the OC concentrations are following patterns similar to those in Fig. 2 (see Sect. 4).

Figure 3 is therefore presenting, for all samples, the contribution of the pyrolysed OC to total OC according to the total OC sample loading. Indeed, there is a tendency to co variations between the two quantities, but the correlation is rather low. Further, the large and systematic differences in the pyrolysed fraction between the samples from winter and summer seasons for a given filter loading (Fig. 3) is another indication that the amount of the pyrolysed fraction is most probably dependant upon OC characteristics and not only dependant upon the respective locations of the deposit and of the laser beam during the thermal analysis. It is out of the scope of this paper to deal in details on the reasons of this result, but some related discussions on the characteristics of the

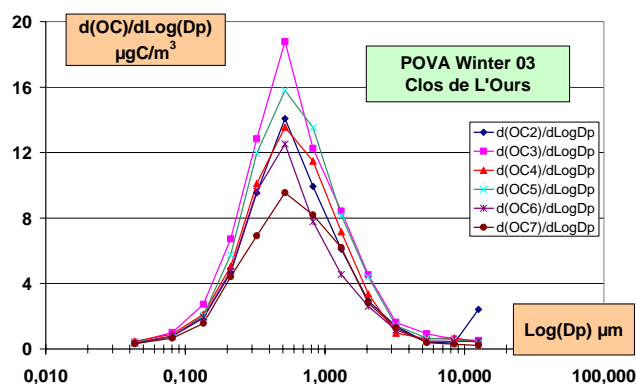


Fig. 6. Daily size distributions of OC concentrations at the “Clos de l’Ours” (suburban Chamonix) during winter 2003.

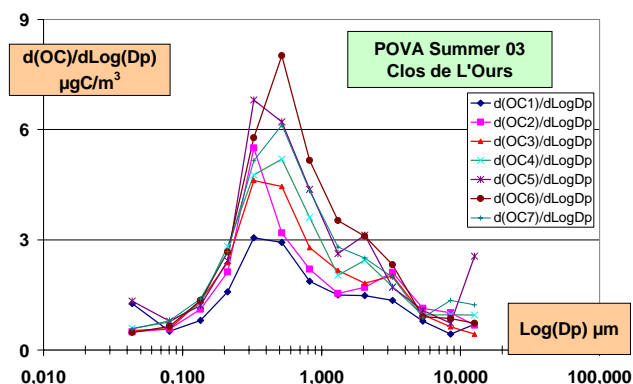


Fig. 7. Daily size distributions of OC concentrations at the “Clos de l’Ours” (suburban Chamonix) during summer 2003.

pyrolysed fraction can be found elsewhere (Yu et al., 2002; Yang and Yu, 2002; Chow et al., 2004). A couple of hypotheses can however be proposed to explain our results. One is that the size of the laser beam (2×4 mm across) could encompass enough spots of the deposit to allow for a proper correction. Another hypothesis could be that the pyrolysed fraction is not located at the actual spots of the deposit, but redistributed over the filter during the first part of the combustion. This is partly substantiated by observations of the colour of the filter of total aerosol sampling at the end of the part of the analysis without oxygen, showing a dark colour even on the back side of the filter (Yang and Yu, 2002; Chow et al., 2004).

Whatever the actual reason, Figs. 2 and 3 indicate that it is not totally irrelevant to use the pyrolysis correction of the TOT method during the analysis of impactor samples. One further step is therefore proposed with Figs. 4 and 5 that present the comparisons of the daily concentrations of OC and EC, respectively, obtained by summing the concentrations of all of the impactor stages in the one hand, and averaging the concentrations of the six 4-h total filtration samples of the same day in the other hand. All sites and campaigns are taken into account. In both cases, the correlation coefficients are excellent, indicating a good proportionality between the two methods. The intercepts are really low, indicating no systematic bias. The slope of the regression is close to 1 in the case of OC, as opposed to slopes of 0.47 (summer) and 0.97 (winter) obtained during the Pittsburgh super site study (Cabada et al., 2004). Such low slopes indicate larger concentration with filter than impactor sampling, that may be due to a larger positive artifact (i.e. adsorption of SVOC) for the filter sampling compared to impactor sampling (cf above). The larger slope in our case may be linked to a lower positive artifact in winter (since the winter samples obtained in Chamonix are driving the correlation in our study) as also reported in the study of Cabada et al. (2004). The slope of the regression between EC concentrations in our study, at 0.76 (Fig. 5), is the same as that proposed in ten

Brink et al. (2004), at 0.71. No information concerning the correlation for EC concentrations is given for the study by Cabada et al. (2004), while a much lower slope is proposed in the study conducted by Viidanoja et al. (2002), estimated close to 0.25 from one of their figures. With no additional insights, we can conclude, like ten Brink et al. (2004), that “the difference in EC between filter and impactor samples is therefore unexplained and deserves additional research”. In this direction, it should be noted that a comparison of black carbon (BC) concentrations obtained with filters and impactor samplings, associated with analyses with the Integrated Sphere technique, led to better results, with a slope of 1.08 for the regression between the two series for urban samples (Hitzenberger and Tohno, 2001).

Overall, these comparisons reveal differences that are well within the uncertainties in the determination of EC and OC concentrations observed for parallel sampling with different methods during INTERCOMP2000 (ten Brink et al., 2004), for example. Then, the final conclusion is that results for EC and OC concentrations obtained with impactor sampling with quartz filters analyzed with the TOT method and taking into account the pyrolysed correction are most probably of a quality not worst than that of most other data sets for concentrations of EC and OC in the literature. Therefore, we can now try to evaluate these results in terms of evolution of the size distributions.

4 Size distributions of EC and OC

Figures 6 and 7 present the overall results obtained for the size distribution of OC at the suburban site (“Le Clos de l’Ours” in Chamonix) during the winter and summer periods, respectively. Despite evolutions of the concentrations from day to day, the shapes of these size distributions remain quite stable for each season and fairly different between the summer and winter periods. The processes leading to overall changes in the concentrations will not be discussed here,

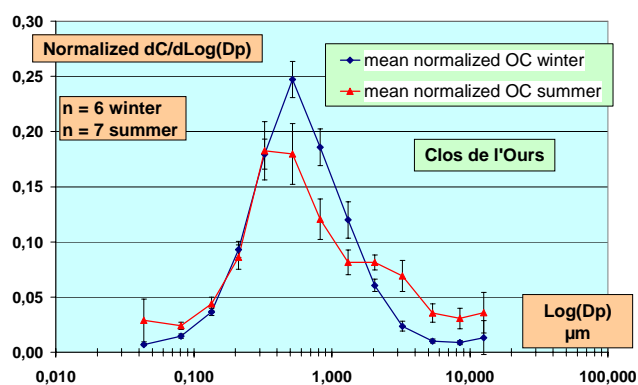


Fig. 8. Average normalized daily size distribution of OC concentrations at the “Clos de l’Ours” (suburban Chamonix) during winter and summer 2003.

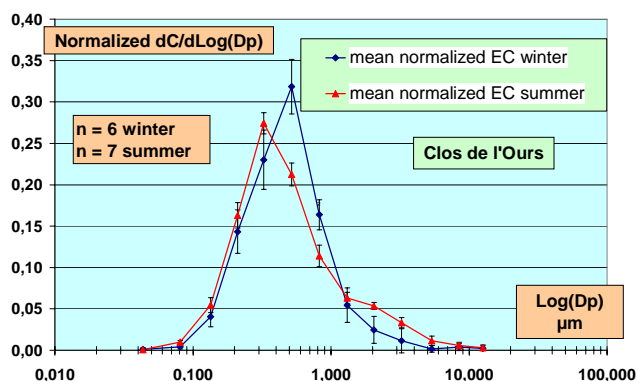


Fig. 9. Average normalized daily size distribution of EC concentrations at the “Clos de l’Ours” (suburban Chamonix) during winter and summer 2003.

but some information on this topic can be found in Aymoz (2005) and Jaffrezo et al. (2005b)¹. Owing to this stability of the size distributions for each sampling campaign, we calculated average size distributions of the concentrations of EC and OC for each campaign and each site. These were obtained by first normalizing the concentration of each impactor stage by the total concentration of that day (i.e., the sum of the concentrations of all impactor stages), then averaging all of these normalized concentrations. Figures 8, 9, 12, and 13 present these normalized concentrations and associated standard deviations for the two sites and the two species.

a) Suburban site

Figure 8 confirms the stability of the size distributions of OC for each campaign at the suburban site, with rather low standard deviations for the normalized concentrations. One can see several changes in the shape of the size distributions from one season to the other. *In winter*, the size distribution is clearly monomodal, with a maximum of the concen-

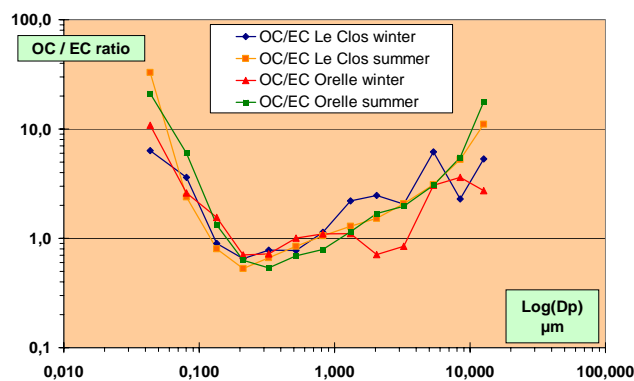


Fig. 10. Average ratios OC / EC for all sites and all seasons.

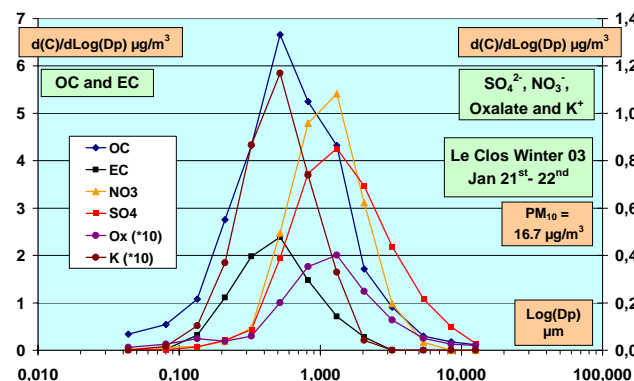


Fig. 11. Daily size distributions of the concentrations of OC, EC, sulfate, nitrate, oxalate and potassium obtained in “Le Clos” (suburban site in the Chamonix Valley) on 21 January 2003.

trations for the impactor stage collecting aerosol with aerodynamic diameters between 0.40 and 0.65 μm . EC concentrations present the very same monomodal shape (Fig. 9), and are also peaking in the same size range. This size range is larger than that typically produced by primary emissions, such as those from diesel (Kerminen et al., 1997) and gasoline (Kleeman et al., 2000) powered cars, the maxima in the mass size distribution being close to 120 nm for both sources. It is also larger than wood-smoke emissions (Hays et al., 2004) that have mass size distributions peaking in the range 120–520 nm depending on the wood. The size range we observed is generally considered as the result of the growth of smaller particles by processes taking place in a hydrated phase (Kerminen and Wexler, 1995) and is often called the droplet mode (John et al., 1990). It is possible that in our case, during the winter campaign, such a processing is taking place locally in the fog that forms at the top of the low inversion layers during the persisting anti-cyclonic conditions observed in the valley. In support of such an hypothesis, the oxalate and other DCA, most probably formed in an aqueous phase (Ervin et al., 2004), were also measured in the same

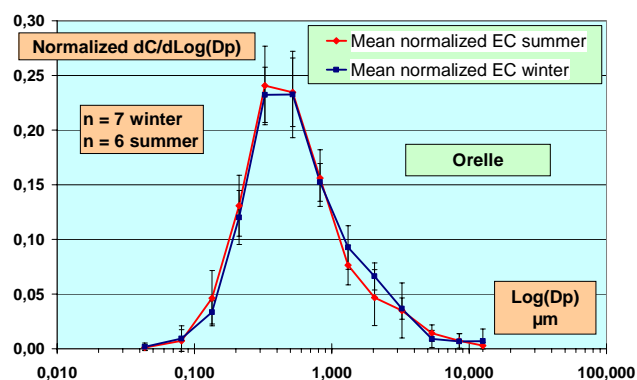


Fig. 12. Average normalized daily size distribution of EC concentrations in Orelle (rural site in the Maurienne Valley) during winter and summer 2003.

samples (not shown) and exists mainly in this droplet mode, albeit with a much lower mass ratio to OC than that found in summer samples. Further, it is striking that the minimum of the OC/EC mass ratio, traditionally used as an indicator of primary emissions (Strader et al., 1999) is at its lowest in a lower size range (ie, 0.17 to 0.26 μm) than this droplet mode for these winter samples (Fig. 10). All of these observations point out to a rapid processing of the local primary emissions leading to growth of the particles with internal mixing of EC and OC. The mass fractions of these species in the size ranges at both ends of the spectrum ($<0.1 \mu\text{m}$ and $>1.0 \mu\text{m}$) are really low.

In summer, the size distributions of OC keep trace of other processes that take place during the aging of the organic aerosol. First, the maximum of the droplet mode is located in a lower size range (0.26 to 0.40 μm) than in winter and the non-Gaussian shape of the peak most probably results from a bimodal distribution with an accumulation and a droplet modes. This is also the case for EC, leading to size distributions for this last species that are in line with several previous studies (Hintzenberger and Tohno, 2001 and reference therein). Overall, these observations most probably indicate less wet processing of the aerosol during aging than in the winter conditions. We can note that these results are in contradiction with those from the study of Cabada et al. (2004) that shows larger sub micron size modes for EC and OC in summer than in winter at the Pittsburgh super site, attributed to a greater influence of primary emissions in winter. Further investigations are needed, but it is likely that the anticyclonic conditions prevailing in the valleys in winter are promoting strong aging processes for a stagnant aerosol.

Second, one can see an increase in the concentration of OC in the smaller size ranges (Aitken mode: 0.03 to 0.10 μm) compared to the winter situation. This increase could result from direct (primary) emissions or from the growth of particles initially in the nucleation mode (diameters below 30 nm), according to processes involving gas/particle conver-

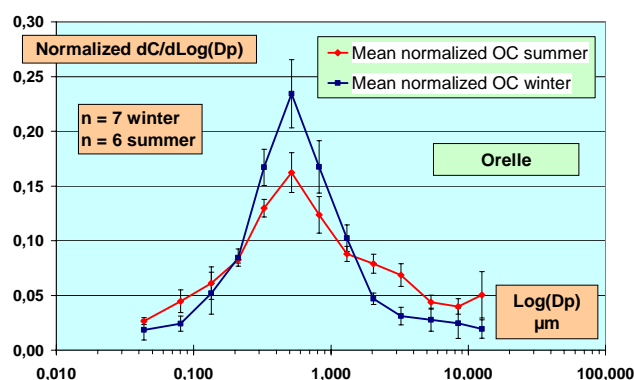


Fig. 13. Average normalized daily size distribution of OC concentrations in Orelle (rural site in the Maurienne Valley) during winter and summer 2003.

sions (Sellegrì et al., 2005). Such a change between winter and summer is only concerning OC, not EC, resulting in a much higher mass ratio OC/EC in summer (average value up to 33 for the smallest particles, Fig. 10) than in winter (average value of 6.4 for the same size range). If this last OC/EC ratio can be found in primary emission of residential wood burning (Schauer et al., 2001) that are common in the valleys in winter (Marchand, 2003; Marchand et al., 2004, 2005²), ratios above 30 are not measured in primary vehicle emissions (Schauer et al., 1999, 2002; Rogge et al., 1993) that represent some of the major sources in summer. All of these observations point out to the strong impact of gas/particle conversion in this size range, as already underlined from summer samples from K-puszt (a rural area) by Temesi et al. (2003).

Third, a distinct formation of a super micron mode can be seen for OC (Fig. 8) in summer, with a much smaller increase of EC concentrations in this size range. By analogy with the case of nitrate, one can make the hypothesis that this increase could result from the adsorption of gaseous precursors at the surface of crustal particles (see below the case of the rural site in summer, Fig. 14). This hypothesis presents implications (that demands further studies) on the processes that would take place in the gas phase and would produce more semi volatile (condensable) products in summer than in winter.

All of these changes indicate that, in this suburban environment, very different processes are taking place during aerosol aging, depending on the season. As a result, the average mass fractions of OC (and of EC, to a lower extent) in each of 3 size ranges (roughly describing the Aitken, accumulation + droplet, and super micron modes) experience large changes between the two seasons (Table 3), the most important being the decrease of the mass fraction of the accumulation + droplet modes.

²Marchand, N., Aymoz, G., Jaffrezo, J.-L., Masclet, P., and Besombes, J.-L.: Biomass burning indicators in the aerosol of Alpine valleys, *Atmos. Chem. Phys. Discuss.*, in preparation, 2005.

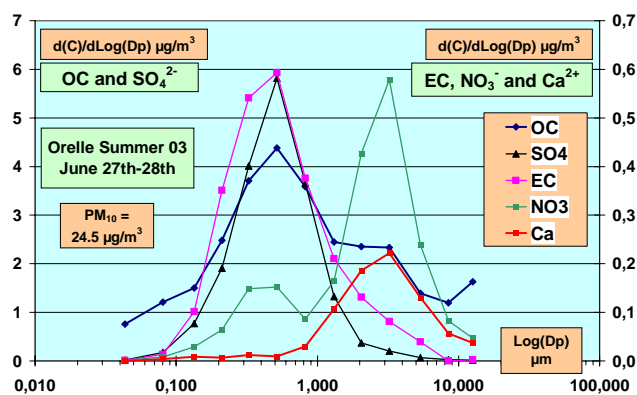


Fig. 14. Daily size distributions of the concentrations of OC, EC, sulfate, nitrate, and calcium obtained in Orelle (rural site in the Maurienne Valley) on 27 June 2003.

However, on a case by case basis, the processes involved are most probably more complex, as exemplified with Fig. 11 presenting the size distributions of EC and OC in parallel with that of some ionic constituents, for a sample obtained in winter conditions (from 21 January 08:00 LT to 22 January 08:00 LT). This figure shows that the mode centred in the interval 0.40 to 0.65 μm (as described earlier) includes OC, EC, and K^+ , this last species being a strong indication of the impact of residential wood burning emissions on the formation of that mode. However, this figure shows another mode, externally mixed with the first one and centred between 1.0 and 1.6 μm that includes nitrate, sulfate, and oxalate. A shoulder in the OC concentrations (but not visible for EC) indicates that some mass fraction of OC is also included in this mode. Another mode in the super micron range exists (centred between 2.5 and 4.0 μm), albeit with a very low mass fraction, as detected with concentrations of calcium of a few ngm^{-3} (not shown). It may include a small fraction of sulfate, as indicated by a shoulder on the right side of the size distribution of this species. We are currently unable to propose any hypothesis to explain the formation processes leading to a mode with diameter between 1.0 and 1.6 μm , dissociated from the droplet mode, even if the nature of the species included (all of them having a secondary origin) points out to aqueous production and/or exchanges between the gas and particle phases. Despite all of this information, it is impossible to affirm whether these distributions are actually induced by some processes during the aging of the aerosol or result from direct emissions. However, it should be noted that it is the only such case, over the full week, of a large shift of sulfate (and other species) towards a mode centred at about 1.5 μm . All other cases are more “classical”, with sulfate mostly located in the accumulation and droplet modes together with EC and OC (see for example Fig. 14).

Table 3. Average mass fraction (%) of EC and OC in each of 3 size ranges for all sampling campaigns.

	OC	EC	OC	EC
	Le Clos winter		Orelle winter	
$D_{\text{aero}} < 0.17 \mu\text{m}$	6	5	9	4
$D_{\text{aero}} > 0.17 \mu\text{m}$ and $< 1.00 \mu\text{m}$	71	86	65	74
$D_{\text{aero}} > 1.00 \mu\text{m}$	24	10	25	22
	Le Clos summer		Orelle summer	
$D_{\text{aero}} < 0.17 \mu\text{m}$	10	7	13	5
$D_{\text{aero}} > 0.17 \mu\text{m}$ and $< 1.00 \mu\text{m}$	57	76	50	76
$D_{\text{aero}} > 1.00 \mu\text{m}$	33	17	37	18

b) Rural site

The size distributions of EC and OC in the rural case are presented in Figs. 12 and 13, respectively. They show several characteristics already described in the previous (suburban) case, but bring additional information. Strikingly, Fig. 12 shows that the average size distributions of EC are totally identical between the summer and winter periods, an indication that the extent of processing of the aerosol (for processes concerning this species) is the same in the two cases. The large submicron mode is most probably resulting from a bimodal shape with fused accumulation and droplet modes. The mass fractions of EC in the size ranges at both ends of the spectrum ($< 0.1 \mu\text{m}$ and $> 1.0 \mu\text{m}$) are really low, with no sign of evolution between seasons (Table 3).

The average OC size distribution in winter (Fig. 13) looks like that at the suburban site in Chamonix, with a maximum in the droplet mode only, and no sign of bimodality with an accumulation mode like for EC. There is no distinct mode in other size ranges, but the mass fractions at both ends of the spectrum ($< 0.1 \mu\text{m}$ and $> 1.0 \mu\text{m}$) are higher than in Chamonix, which may underline some extent of processing by gas/particle exchanges during transport to the site, even in winter situations. The influence of these last processes is clearly visible in the change of the average size distributions from winter to summer with, like in Chamonix, larger mass fractions in the Aitken and the super micron modes in summer (Fig. 13 and Table 3). Compared to the suburban case, the shift of the droplet mode for OC towards the accumulation mode is smaller, and the increase of the mass fraction in the Aitken mode is larger. All of these observations represent indications of further aging than in the suburban case. Conversely, the increase of the mass fraction of OC from winter to summer in the super micron mode is identical for samples obtained at the two sites.

Figure 14 gives an example of a summer daily size distributions, for EC, OC, and some ionic species of interest for the understanding of the processes involved. This sample shows a structure of the sub micron size distribution

dominated by the droplet mode, which includes large amounts of sulfate, OC, EC, and nitrate. Shoulders on the left side of this mode indicate an accumulation mode that comprises some EC, OC, nitrate, but apparently only a very small amount of sulfate. The Aitken mode is well developed and apparently includes only OC, with minimal contribution from sulfate or any other species mentioned. This last point was also noted in Pasadena (CA, USA) in a study conducted in February, with much larger concentrations of OC than sulfate in the ultrafine (0.056 to 0.097 μm) size range (Hughes et al., 1998). The shape of the super micron mode is well described by the evolution of calcium concentrations, with a peak in the diameters between 2.5 and 4.0 μm . Associated with that species from a crustal origin, one can find the larger mass fraction of nitrate, as well as a large fraction of OC. No sulfate is included in that mode, an indication that the processes involved in its evolution may not include any wet phase but are dominated by gas/particles exchanges.

Overall, as also indicated by average values in Table 3 and Fig. 10, these evolutions of the size distributions are in line with further impact of the aging processes (gas/particles exchanges, addition of mass in the droplet mode) from the suburban case to the rural one.

5 Conclusions

Collections of samples were conducted for the determination of the size distributions of EC and OC during the intensive sampling campaigns of the POVA program, in two Alpine valleys of the French Alps, in summer and in winter. The comparison of concentrations obtained for samples collected in parallel with impactor- and filter-based methods indicates that the correction of pyrolysis seems to work for the impactor samples despite non even deposits.

The size distributions of the concentrations of EC and OC present large variations between winter and summer, and between a suburban and a rural site. In winter, an overwhelming proportion of the mass fraction of both species is found in the droplet and accumulation modes, often (but not always) in association with sulfate and with other chemical species resulting from secondary formation processes. Some indications of gas/particles exchanges can be found for the other parts of the size spectrum (the Aitken and super micron modes) in the case of the rural site. In summer, the changes are more drastic with, according to the case, a dominant droplet or accumulation mode. Particularly at the rural site, the large extent of processing of the aerosol due to gas/particles exchanges is evident for the Aitken and super micron modes, with increasing of the OC mass fractions in these size ranges. All of these observations give indications on the degree of internal vs. external mixing of the species investigated in the different modes.

Further experiments are needed, including measurements of the total surface size distribution, to investigate the pro-

cesses involved in the gas/particle exchanges, particularly for the super micron mode. These may need to be conducted while taking into account the diurnal changes in atmospheric temperature and relative humidity, and also with an evaluation of the water content of the aerosol in the various size ranges. Finally, specific investigations on molecular species composing OC can lead to further insights into the processes involved in the evolution of the different modes during aging.

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